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DIFFERENTIATION POSSIBILITIES OF PRIMARY AND SECONDARY ORGANIC MATTERS IN THE NEOGENE SEDIMENTS OF THE SOUTH GREAT PLAIN (HUNGARY)

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ABSTRACT

The present paper suggests a method to differentiate the organic matter of primary and secondary character on the basis of the investigations of core samples of two deep-bores drilled in the Neogene sediments of the South Great Plain (Hungary). The two deep-bores are located in the "Hódmezővásárhely—Makó" trench. On the basis of the investigation of the soluble organic matter content of the rock types of clay-marl, lime-marl and aleurite it could be stated that the strata sequences of the bores Makó-1 and Hód-1 can be divided into three great units out of which the lower one contains the Tortonian and the predominantly pelitic sequence of the Lower Pannonian being in accordance with the deep-structure; these can be regarded one unit. The middle part is of Lower Pannonian, the upper one of Upper Pannonian age. On the basis of the bitumen content the bore of Hód-1 represents a neritic-pelagic environment while the bore Makó-1, is of near-shore location. As to the suggested method is was also stated that the soluble organic matter of the Lower Pannonian is rather of secondary character, and the hydrocarbon genesis of the same features took place in the Upper and Lower Pannonian while this proved to be dissimilar in the Miocene.

CHANGE OF THE SOLUBLE ORGANIC MATTER CONTENT AS A FUNCTION OF DEPTH

Investigation methods

The soluble, non-volatile organic matter content of the core samples of bores drilled in the "Hódmezővásárhely—Makó" trench was investigated. The part of the disperse organic matter which can be extracted by organic solvents, i.e. the so-called bitumen content was extracted by means of the SOXHLET apparatus. Subsequent extractions were applied: the rock sample was first extracted by chloroform to obtain the bitumen-A, and after dissolution by hydrochloric acid the extraction with benzene-ethanol was carried out. The extract obtained in this way is called bitumen-C (in the following: Bit-A and Bit-C). The extracts Bit-A and Bit-C were divided into three fractions by means of column chromatography. To characterize the relation between the bitumen values and depth calculation of regression was carried out concerning the whole investigated strata sequence as well as separatedly in case of the Upper, Lower Pannonian and Miocene samples. This computation has been necessary since the tendency of change can be incompletely followed because of the fluctuation of the values.

Change of Bit-A and Bit-C as a function of depth in the bore Makó-1

The Bit-A values of the core samples of the bore Makó-1 varies between $20 \cdot 10^{-3}$ and $61 \cdot 10^{-3}$ per cent. In three samples it shows very high values: in 2500 metres $56 \cdot 10^{-3}$ per cent, in 1400 metres $48 \cdot 10^{-3}$ per cent and in 3180 metres $61 \cdot 10^{-3}$

per cent (*Fig. 1* and Table 1). On the basis of regression computed to the investigated sequence of strata the value of Bit-A increases with increasing depth. This corresponds to the statement of JEREMENKO [see: MEINHOLD, 1965] as to which the quantity of neutral bitumen increases with the age. When having computed these values to the individual Upper and Lower Pannonian samples the regression lines have shown decreasing tendency as a function of depth. Because of the small value of the regression coefficient this decrease is very slight, in case of the Lower Pannonian samples the Bit-A is practically independent of depth. On the basis of regression at the boundary of the Lower and Upper Pannonian the quantity of Bit-A shows a sudden increase. This may be connected with the more progressive measure of the continuous transformation of the organic matter and with the strengthening of the secondary character of Bit-A. All these correlate with the change in sedimentary environment fixed by the geologists at the boundary of the Upper and Lower Pannonian.

The value of Bit-C shows considerably greater fluctuation than that of Bit-A, its quantity varies from $20 \cdot 10^{-3}$ to $140 \cdot 10^{-3}$ per cent. Its value is extremely high in 1000 metres ($69 \cdot 10^{-3}$%), in 1400 metres ($69 \cdot 10^{-3}$%), in 2100 metres ($140 \cdot 10^{-3}$%), in 2200 metres ($106 \cdot 10^{-3}$%) and in 3180 metres ($74 \cdot 10^{-3}$%). On the basis of the regression line the value of Bit-C decreases with increasing depth, probably as a result of the Bit-C→Bit-A transformation (*Fig. 2* and Table 1).

According to the investigations of TISSOT [1971] the quantity of the hetero-compounds of great molecular weight decreases with increasing depth because of the formation of the compounds poor in heteroelements or being totally in lack of these. He assumed that the following transformation takes place:

Kerogen → compounds containing O, N, S heteroelements (acidic bitumen) → hydrocarbons, resins, asphalts (neutral bitumen).

Similar transformation is referred by the experiments of LOUIS and TISSOT [1967] carried out on samples originating from the Paris-Basin. They treated the

TABLE 1

Bitumen contents of the core samples of the bore Makó-1

No.	Depth	Bit-A $\cdot 10^{-3}$	Bit-C $\cdot 10^{-3}$	Rock type
1	805,30— 808,00	21	38	clay-marl
2	1000,00—1006,00	39	68	clay-marl
3	1100,50—1102,70	36	31	clay-marl
4	1403,50—1404,05	29	63	aleurite
5	1404,50—1405,10	48	69	clay-marl
6	1500,10—1501,50	23	20	aleurite
7	2102,20—2102,40	25	140	aleurite
8	2150,00—2150,80	32	25	aleurite
9	2196,00—2196,50	31	106	aleurite
10	2351,00—2352,05	34	49	aleurite
11	2500,14—2500,21	46	51	aleurite
12	2722,00—2722,35	24	51	clay-marl
13	3064,45—3064,51	38	23	clay-marl
14	3180,15—3180,20	61	64	clay-marl
15	3290,00—3290,20	38	48	clay-marl
16	3490,37—3490,42	32	24	clay-marl
17	3951,83—3952,00	33	29	clay-marl

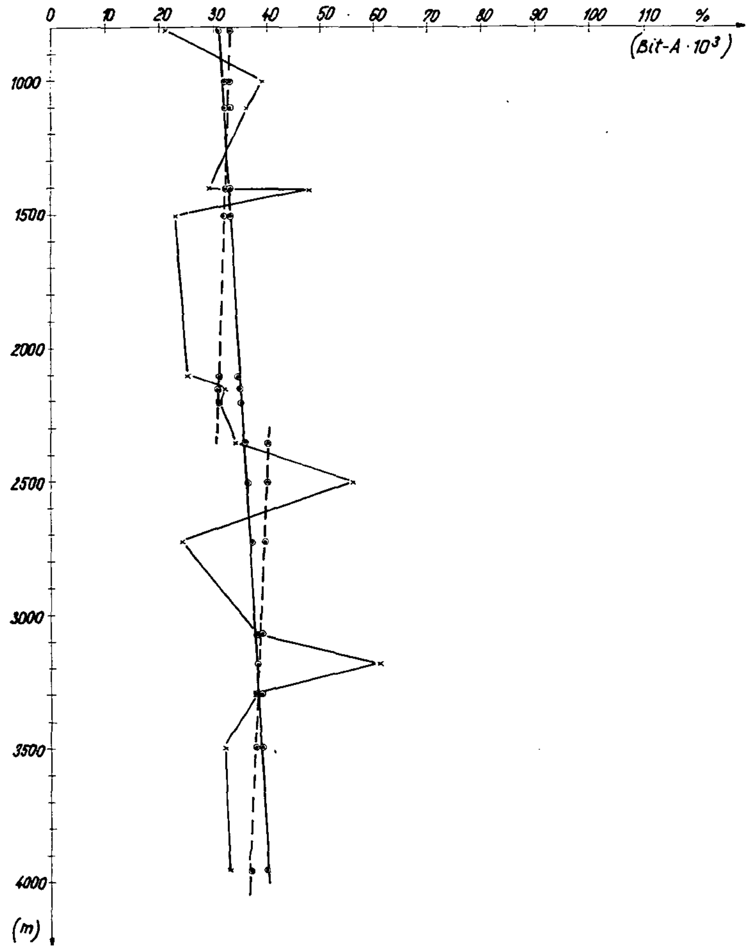

Fig. 1. The values of Bit-A from the Makó-1 drilling in the function of the depth

rock samples with such pressure and temperature values which are predominant in the deeper parts of the basin. They observed the increase of the quantity of neutral bitumen and assumed this process to take place through the formation of acidic bitumen.

In our investigations the Bit-C corresponds to the acidic, the Bit-A to the neutral bitumen; consequently, after TISSOT the kerogen → Bit-C → Bit-A transformation is supposed.

On the basis of the investigation of core samples this transformation cannot be followed in such an unambiguous manner. The quantities of Bit-A and Bit-C of the single samples are influenced by the environmental factors, the quantity of the organic matter of the sediment, the quality and accidental migration of the organic components.

Regarding the computation carried out separatedly on the Upper and Lower Pannonian samples the value of Bit-C increases in the Upper Pannonian and decreases in the Lower Pannonian samples. This may probably be connected to the consecutive feature of transformation, in the Upper Pannonian the transformation of kerogen → Bit-C, in the Lower Pannonian that of Bit-C → Bit-A could follow.

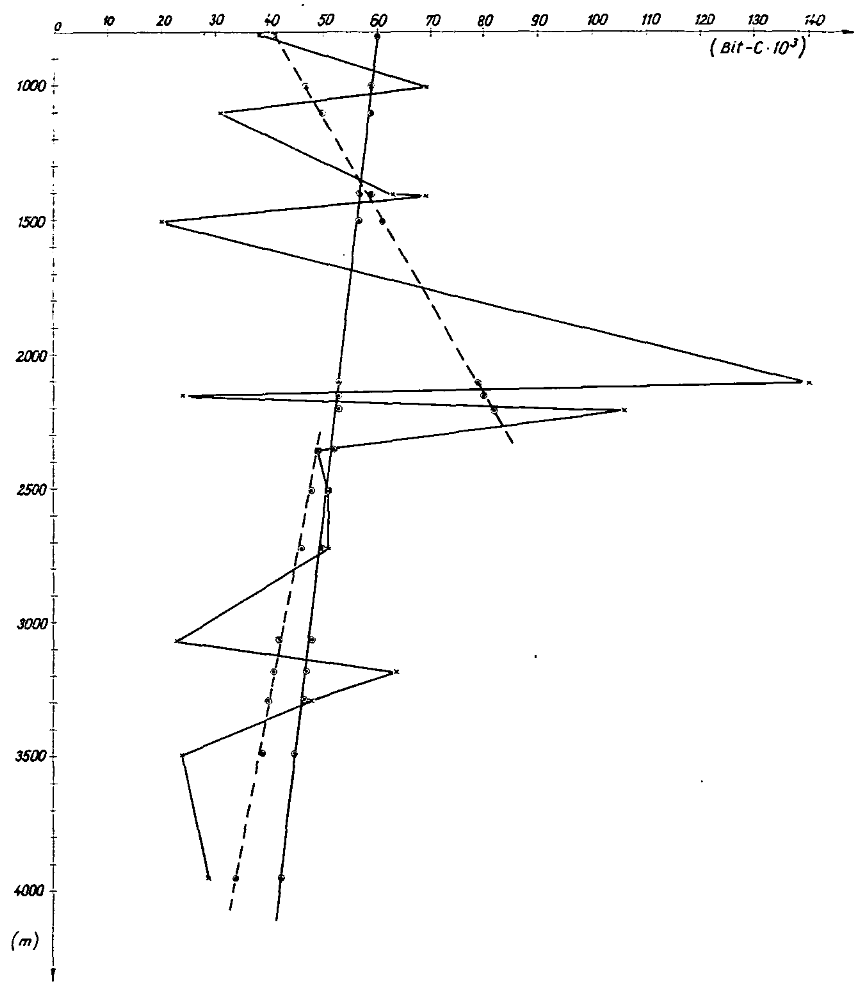

Fig. 2. The values of Bit-C from the Makó-1 drilling in the function of the depth

Change of Bit-A and Bit-C as a function of depth in the bore Hód-1

The bore Makó-1 did not reach the Miocene strata while the bore Hód-1 located NW of it in a distance of about 5 km was stopped in Miocene formations. Out of the core samples of the bore of Hód-1 two samples of the Upper Pannonian were investigated which alone could not be evaluated thus it was carried out only together with the Lower Pannonian ones.

The quantity of Bit-A varies between $14 \cdot 10^{-3}$ and $249 \cdot 10^{-3}$ per cent. Extremely high values were obtained in 4264 m ($95 \cdot 10^{-3}$), in 4538 m ($115 \cdot 10^{-3}$) and in

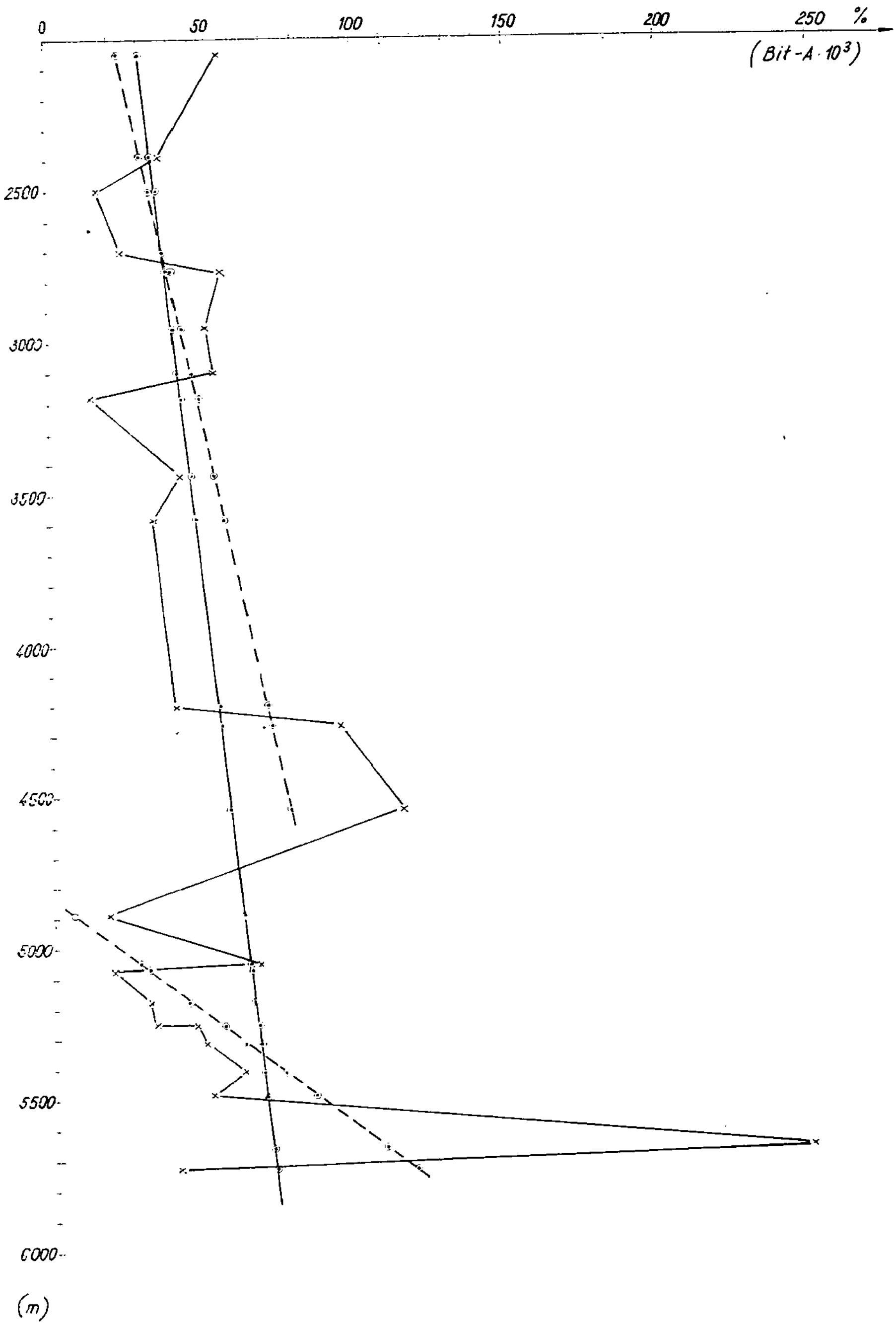

Fig. 3. The values of Bit-A from the Hód-I drilling in the function of the depth

TABLE 2

Bitumen contents of the core samples of the bore Hód-1

No.	Depth	Bit-A $\cdot 10^{-3}$	Bit-C $\cdot 10^{-3}$	Rock type
1.	2050,57—2050,66	56	69	clay-marl
2.	2386,44—2386,65	37	53	clay-marl
3.	2501,62—2501,68	17	67	fine aleurite
4.	2700,85—2701,04	24	59	fine aleurite
5.	2759,17—2759,40	56	48	clay-marl
6.	2954,17—2954,27	52	69	fine aleurite
7.	3098,00—3099,00	54	64	clay-marl
8.	3182,20—3182,60	14	53	clay-marl
9.	3437,30—3438,30	43	46	clay-marl
10.	3584,50—3584,80	34	58	clay-marl
11.	4200,00—4200,40	40	49	fine aleurite
12.	4264,65—4264,75	95	55	fine aleurite
13.	4538,32—4538,78	115	56	marl
14.	4888,45—4888,60	18	98	aleurite
15.	5054,51—5054,60	67	125	clay-marl
16.	5072,72—5072,94	19	122	lime-marl
17.	5174,15—5174,32	31	109	lime-marl
18.	5252,52—5252,68	46	97	lime-marl
19.	5255,71—5255,89	33	71	marl
20.	5311,39—5311,43	49	77	lime-marl
21.	5407,30—5407,45	62	79	lime-marl
22.	5483,43—5483,60	51	106	lime-marl
23.	5660,64—5660,80	249	225	lime-marl
24.	5732,11—5732,28	40	109	marl

5660 m ($249 \cdot 10^{-3}$). On the basis of regression computed to the whole investigated sequence the value of Bit-A is increasing similarly to the bore Makó-1 (*Fig. 3,* Table 2). Taking the separate computation to the Lower Pannonian and Miocene samples it can be stated that the quantity of Bit-A increases both in the Lower Pannonian and in the Miocene. This increase is of much higher degree within the Miocene than in the Lower Pannonian (tg $\alpha = 2.16 \cdot 10^{-5}$ and $13.31 \cdot 10^{-5}$). In the Lower Pannonian the secondary character resp. transformation-degree of the bitumen is probably increasing. This is the same in the Miocene, too, with the difference that primary bitumen is replaced by secondary one.

The boundary between the Lower Pannonian and Miocene was drawn between 4550 and 4850 metres since on the basis of the bitumen content the change follows in this depth interval which is extraordinarily conspicuous in case of the Bit-C values. This delineation is supported by the statement of K. SZENTGYÖRGYI [1973], according to which in the Lower Pannonian sequence much sandstone can be taken into consideration down to 4450 metres.

The structure of the strata sequence changes from 4450 metres, this section is characterized by the frequent alternation of thin sandstone, aleurite and clay-marl. The proportion of sandstones decreases. The Tortonian sediments show similar petrographic formations. These factors are, however, significant from the point of view of the organic matter.

The value of Bit-C varies between $46 \cdot 10^{-3}$ and $225 \cdot 10^{-3}$ per cent. It produces extreme values in 5054 and 5660 metres of $125 \cdot 10^{-3}$ resp. $225 \cdot 10^{-3}$ per cent (*Fig. 4.* and Table 2). On the basis of regressions the tendency of changes increases regarding the whole sequence, in the Lower Pannonian decreases, and in the Miocene increases.

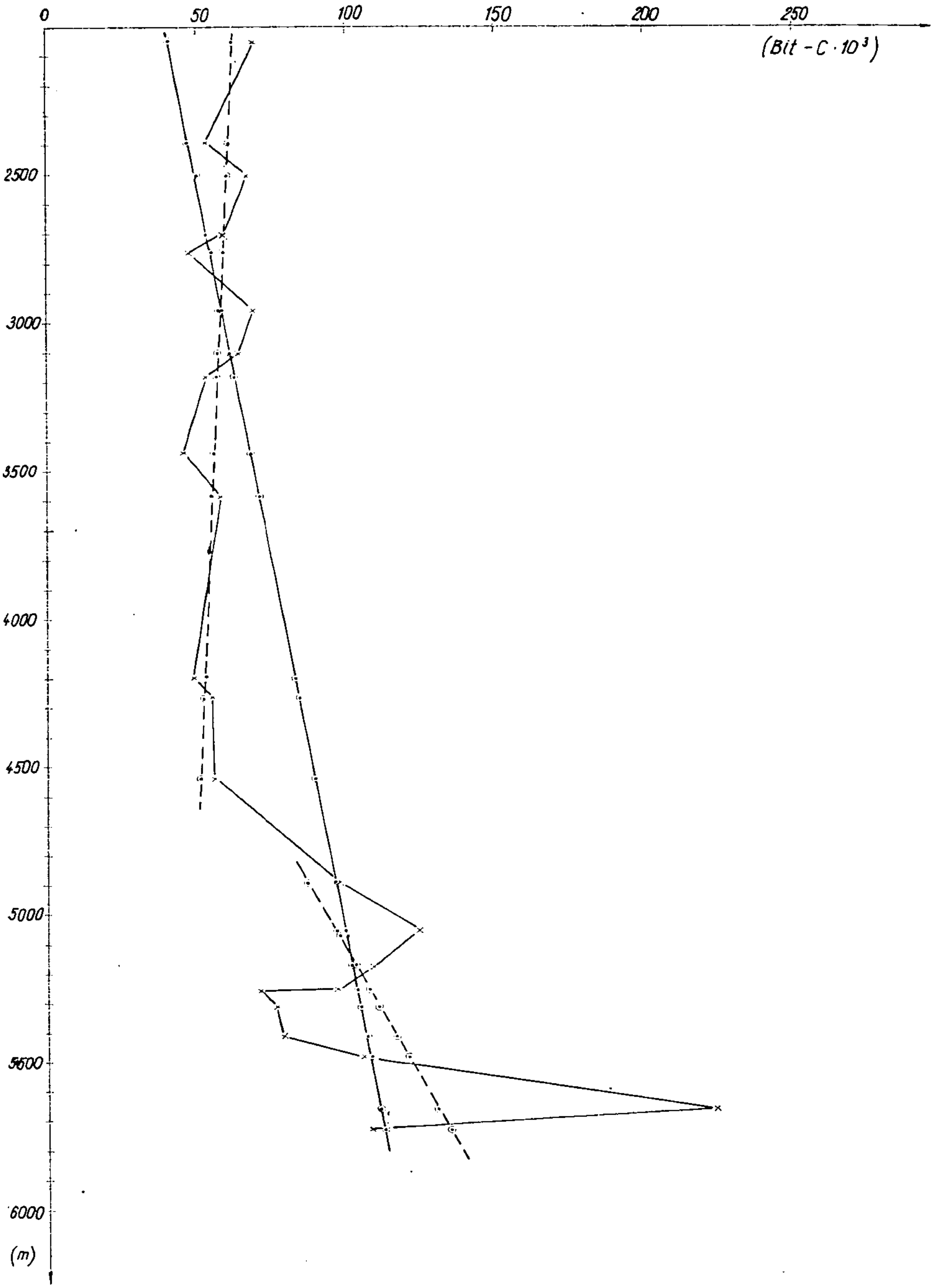

Fig. 4. The values of Bit-C from the Hód-I drilling in the function of the depth

As to our assumption this decrease can be attributed to the strengthening of the Bit-C→Bit-A process as a result of the consecutive character of the Bit-A formation process, as it has been characteristic also of the Lower Pannonian samples of the bore Makó-1. On the contrary, the increase following in the Miocene may relate to progression of the formation process of Bit-A. The quantity of bitumens extracted from the samples of the bore Hód-1 is greater than in case of the bore Makó-1. This difference in quantities can be traced back to the location of the bores in the sedimentary basin. On the basis of the bore Hód-1 in the "Hódmezővásárhely—Makó" trench a pelagic facies of several metres depth of water, of H_2S-content and of negative redox potential existed [M. MUCSI, 1973]. The bore Makó-1 is of near-shore position while the Hód-1 bore lies farther from the shore, as it can be proved on the basis of bitumen content.

POSSIBILITY OF DISTINCTION OF PRIMARY AND SECONDARY CHARACTER OF THE SOLUBLE ORGANIC MATTER

The change of the quantity of Bit-A and Bit-C has till now explained by the thermal degradation of the organic matter. It is not enough to take into consideration the chemical transformations took place in the organic matter; as regarding the explanation of the changes since as it was mentioned above other factors may also play decisive role in the quantitative formation of the organic matter. One of these factors is the migration itself thus in the course of the investigation we tried to obtain some information on the primary resp. secondary character of the organic matter.

As to our assumption to decide the primary resp. secondary character of the organic matter, the quotient Bit-C/Bit-A can be applied completing with the values Bit-A and Bit-C. Since Bit-A is a much more mobile component, in the places where the organic matter can be considered to be of secondary character the Bit-A value should reach a maximal value.

Owing to its more polar character, the Bit-C is capable to adsorption and is bound rather to its formation place, thus, it can be assumed that its greater quantity relates to the primary character of the organic matter. When this assumption can be accepted within certain limits, the value of the quotient Bit-C/Bit-A will be low in case of primary, and high in case of secondary organic matter and this can be connected with the mobility of Bit-A and *in situ* character of Bit-C. The quotient alone is insufficient to decide this problem since in the case when both the Bit-A and the Bit-C values are high, i.e. the value of the quotient does not differ from the average, the presence of organic matter of secondary character is improbable in the samples (though the quotient value relates to this fact). Consequently, taking into consideration the values of Bit-A and Bit-C it can be said that the high Bit-C/Bit-A value relates to the primary, the low Bit-C/Bit-A value to the secondary character of the organic matter. Ideally primary and secondary character was found in any core samples, either, thus the terms "primary" and "secondary" refer to predominantly primary and predominantly secondary characters. Between these two extreme stages a medium one can be distinguished which, on the basis of the relative quantitites of Bit-A and Bit-C could be classified as "rather primary" and "rather secondary" categories.

Taking into account all these factors it can be stated that in case of the bore of Makó-1 the organic matter can be considered to be of primary character in the samples of aleurite and clay-marl type deriving from 1403 m (4), 2102 m (7), 2196 m (9) and 2722 m (12); while the samples of aleurite and clay-marl type deriving from 1100 m

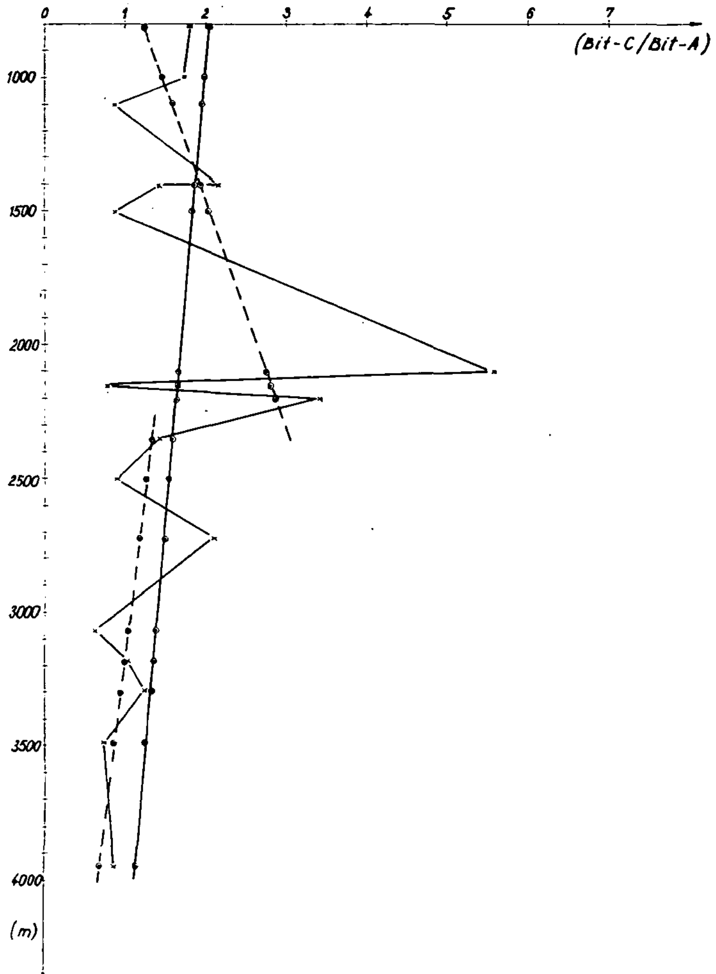

Fig. 5. The values of Bit-C/Bit-A from the Makó-1 drilling in the function of the depth

(3), 2351 m (10), 2500 m (11), 3064 m (13) and 3290 m (15) can be regarded secondary types. In the other samples both the primary and the secondary character can be determined. Within these samples, however, the "rather primary" and "rather secondary" character can be distinguished. *E.g.* in the aleurite and clay-marl samples though containing both types the primary character is predominant in 805 m (1), 1000 m (2), 1404 m (5) and 3180 m (14). In case of the bore Makó-1 the change of the quotient Bit-C/Bit-A with the depth resp. the run of the regression lines are shown in *Fig. 5.*, their values are listed in Table 3.

Based on the regression line, the value of the quotient decreases with increasing depth and this relates to the weakening of the primary and gradual predominancy of the secondary character. In the Upper Pannonian the value of Bit-C/Bit-A is greater than in the Lower Pannonian and increases parallel with the depth, thus in

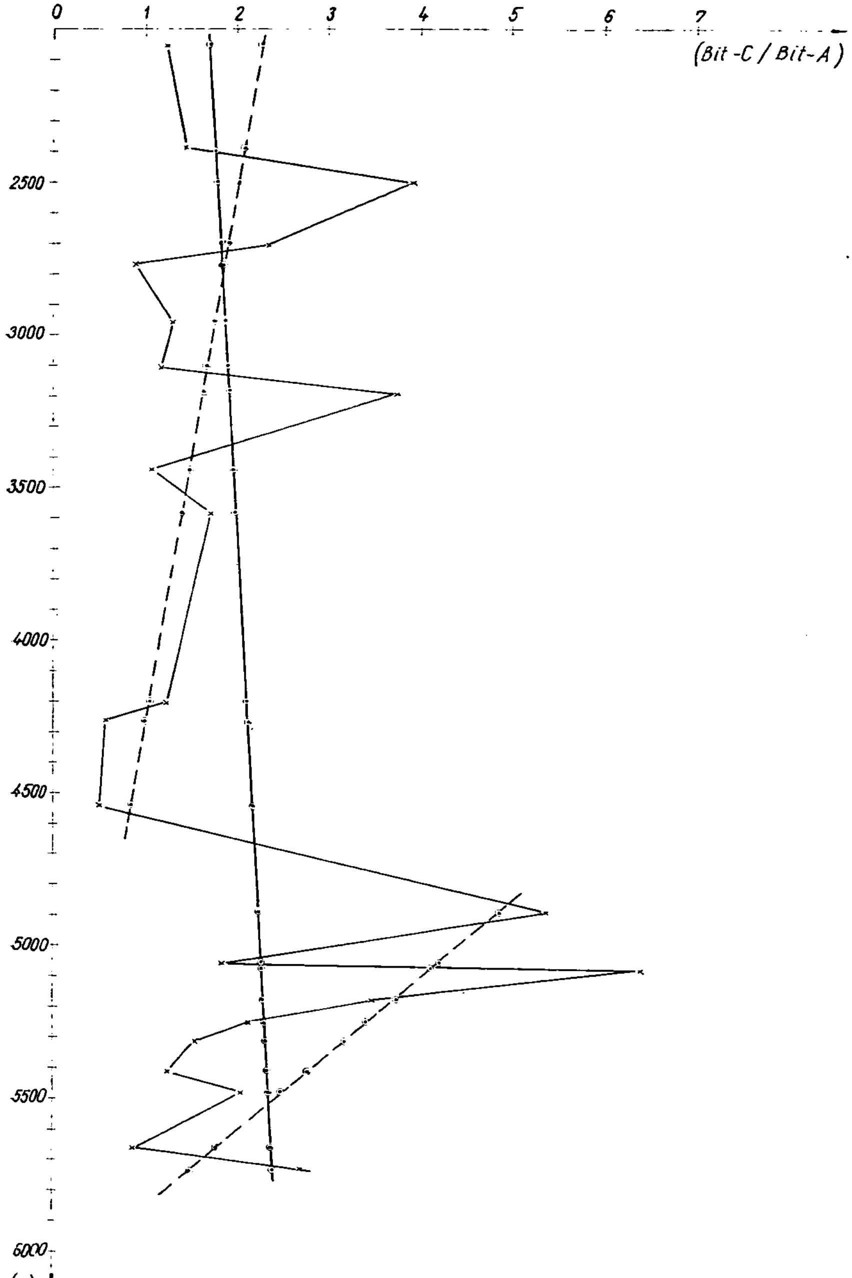

Fig. 6. The values of Bit-C/Bit-A from the Hód-I drilling in the function of the depth

TABLE 3

Bit-C/Bit-A values of the bores Makó-1 and Hód-1

Bore	No.	Bit-C/Bit-A	Bore	No.	Bit-C/Bit-A
M-1	1	1,81	Hód-1	1	1,23
M-1	2	1,74	Hód-1	2	1,43
M-1	3	0,86	Hód-1	3	3,94
M-1	4	2,17	Hód-1	4	2,36
M-1	5	1,44	Hód-1	5	0,85
M-1	6	0,87	Hód-1	6	1,30
M-1	7	5,60	Hód-1	7	1,18
M-1	8	0,78	Hód-1	8	3,78
M-1	9	3,42	Hód-1	9	1,07
M-1	10	1,44	Hód-1	10	1,71
M-1	11	0,91	Hód-1	11	1,23
M-1	12	2,12	Hód-1	12	0,58
M-1	13	0,61	Hód-1	13	0,50
M-1	14	1,05	Hód-1	14	5,44
M-1	15	1,26	Hód-1	15	1,86
M-1	16	0,75	Hód-1	16	6,10
M-1	17	0,87	Hód-1	17	3,51
			Hód-1	18	2,11
			Hód-1	19	2,15
			Hód-1	20	1,57
			Hód-1	21	1,27
			Hód-1	22	2,08
			Hód-1	23	0,90
			Hód-1	24	2,73

the Upper Pannonian the value of the quotient is lower, decreases parallel with the depth, consequently the organic matter is rather of secondary character.

On the basis of the same aspects in the rock samples of fine aleurite, clay-marl and marl type the organic matter could be assigned to the secondary types in 2050 m (1), 2759 m (5), 2954 m (6), 3098 m (7), 4264 m (12) and 4538 m (13), while in the samples of clay-marl, marl and lime-marl type the organic matter is of primary character in 4888 m (14), 5072 m (16), 5174 (17), 5252 m (18) and 5732 m (24). In the transitional category, in the samples of clay-marl, lime-marl type the organic matter is rather of secondary character in 2386 m (2), 3437 m (9), 3584 m (10), 4200 m (11), 5311 m (20) and 5660 m (23), while in the samples of fine aleurite, clay-marl, marl, lime-marl type the organic matter is rather of primary character in 2501 m (3), 2700 m (4), 3182 m (8), 5054 m (15), 5255 m (19) and 5483 m (22). The values of the quotient are listed in Table 3, and are shown as a function of depth in *Fig. 6.* On the basis of the regression computed to the whole sequence the value of the quotient increases with increasing depth which may relate to the strengthening of the bitumen's primary character. In the Lower Pannonian the decrease means the strengthening of the secondary character down to the predominantly pelitic phase, the decrease from this level means the weakening of the primary character from the top downward. In general, it can be said that in the Lower Pannonian the organic matter of rather secondary type predominates in the core samples of both of the bore Hód-1 and Makó-1.

As it was mentioned above according to the kerogen→Bit-C→Bit-A transformation a genetic relation can be assumed between Bit-A and Bit-C. Owing to the other factors influencing the quantity of organic matter this relation cannot be

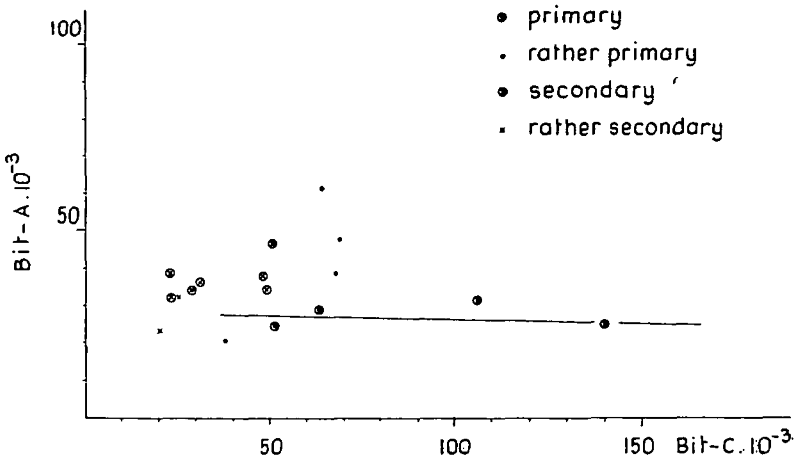

Fig. 7. The values of Bit-A from the Makó-1 drilling in the function of the Bit-C

unambiguously followed. On the basis of the factors used to decide the primary or secondary character of the organic matter a relation between Bit-A and Bit-C was found when taking into account the samples of primary character. In case of the bore Makó-1 plotting Bit-A as the function of Bit-C the points fall onto one straight line *(Fig. 7)*. Out of the samples belonging to the primary category of the transitional group the samples 14 and 5 are exceptions because of the stronger effect of the secondary character.

In case of the bore Hód-1 the samples containing primary organic matter lie along two straight lines *(Fig. 8)*. Taking into consideration the distribution according to ages it can be stated that the straight line of greater rise is accompanied by the

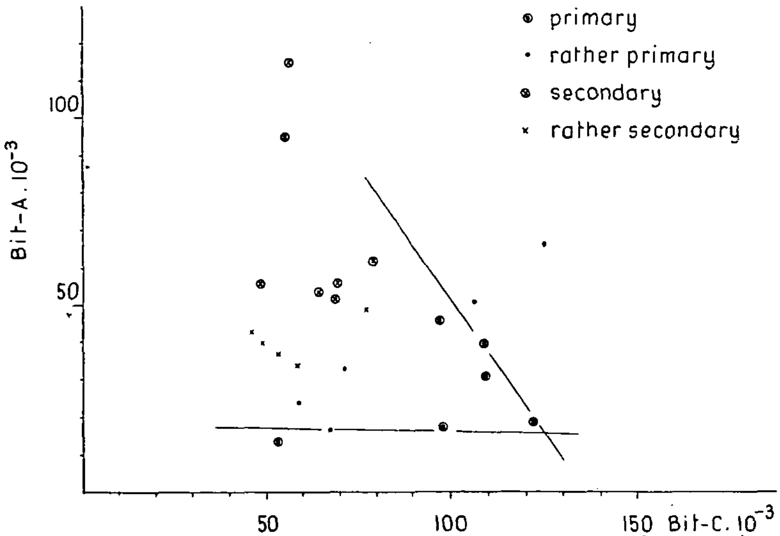

Fig. 8. The values of Bit-A from the Hód-I drilling in the function of the Bit-C

Miocene that of smaller rise by Lower Pannonian samples. From the bore Makó-1 Upper and Lower Pannonian samples were investigated. In case of the samples of Upper and Lower Pannonian age of both drills the rise of the straights are nearly of the same rise *(Figs. 7 and 8)*, from which the hydrocarbon genesis of similar character can be concluded. On the basis of the two straights obtained in the core samples of the bore Hód-1 it can be assumed that in the Miocene and in the Lower Pannonian hydrocarbon genesis of different character took place.

As a result of the migration of the organic matter not only the value of the Bit-C/Bit-A quotient is changing but a relative difference occurs also in the composition of the bitumens. This can be explained by the difference of mobility of the fractions obtained after the column chromatographic separation of bitumens (fraction I is the

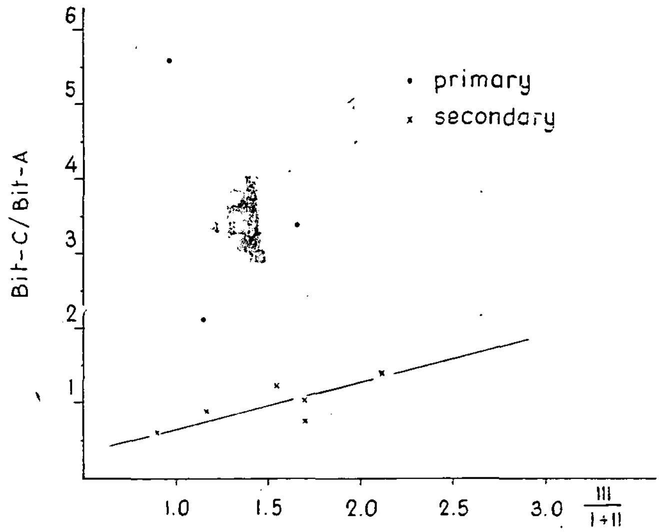

Fig. 9. The values of Bit-C/Bit-A from the Makó-1 drilling in the function of the III/I+II

most mobile, fraction III is least mobile, the hydrocarbons, neutral resins and acidic resins are contained by the I, II and III fractions). It is to be noted that the separation by column chromatography was carried out in the samples in which this proved to be possible as regarding the quantity of the organic matter.

The investigations of GY. GRASSELLY and M. HETÉNYI [1974] relate to the changes deriving from the different mobilities of the fractions, and these emphasized the primary character of the relation between C_{org} and the organic matter of greater molecular weight and containing also heteroelements and extracted by solvent mixture.

They stated that the quantity of chloroform bitumen extracted from sandstones (where the bitumen is certainly of secondary origin) is great, out of the fractions the first is predominating. As to their investigation results in addition to the quantity of chloroform bitumen the column chromatographic fraction can also be used to decide the primary and/or secondary characters of bitumens.

On the basis of all these factors and theoretical considerations the Bit-C/Bit-A quotient should be in connection with the quotient of fractions: III/I+II (see Table

TABLE 4

III/I+II values of the bores Makó-1 and Hód-1

Bore	No.	III/I+II	Bore	No.	III/I+II
M-1	8	1,70	Hód-1	3	1,55
M-1	9	1,65	Hód-1	4	1,11
M-1	10	2,11	Hód-1	5	1,67
M-1	11	1,17	Hód-1	6	1,60
M-1	12	1,14	Hód-1	7	1,45
M-1	13	0,90	Hód-1	8	0,56
M-1	14	1,70	Hód-1	9	1,22
M-1	15	1,55	Hód-1	10	1,33
M-1	16	1,15	Hód-1	11	0,97
M-1	17	2,17	Hód-1	12	0,63
			Hód-1	13	0,43
			Hód-1	14	0,86
			Hód-1	15	0,21
			Hód-1	19	0,80
			Hód-1	20	0,99
			Hód-1	21	1,63
			Hód-1	22	0,49
			Hód-1	23	0,22
			Hód-1	24	0,63

4). In case of both drills plotting the Bit-C/Bit-A as a function of fractions III/I+II, the samples of organic matter of secondary character lie along a straight line (*Figs. 9* and *10*) which may prove the relation between the two quotients in case of the changes followed during migration.

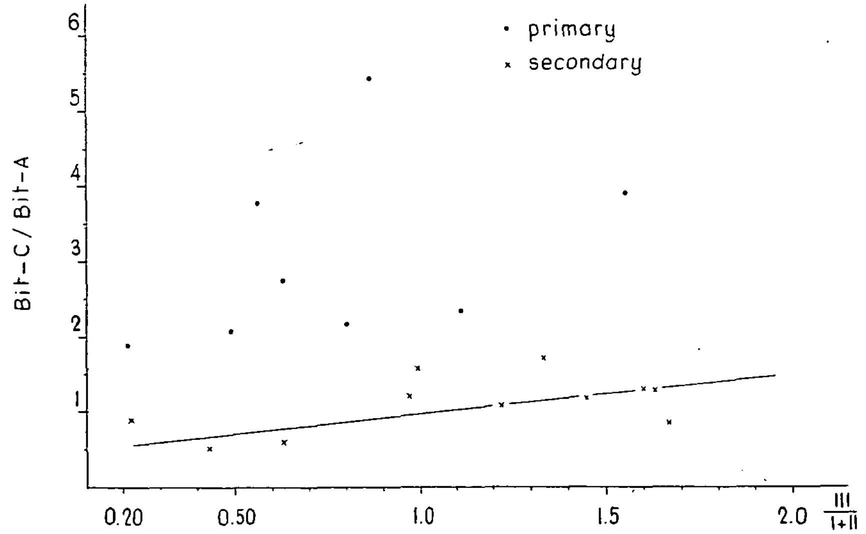

Fig. 10. The values of Bit-C/Bit-A from the Hód-I drilling in the function of the III/I+II

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